

IN SITU IRIDIUM L_{III}-EDGE X-RAY ABSORPTION SPECTROSCOPY OF ELECTRODEPOSITED IRIDIUM OXIDE FILMS IN AQUEOUS ELECTROLYTES

Yibo Mo, Ionel C. Stefan and Daniel A. Scherson

Department of Chemistry
Case Western Reserve University, Cleveland, OH 44106

INTRODUCTION

Iridium oxides display interesting electrochemical characteristics with applications ranging from electrocatalysis, electrochromism, and sensors to charge storage and neural stimulation.[1] Despite years of research, certain aspects of the structure of this material as a function of oxidation state still remain to be elucidated. Much of the controversy stems from variations in the response of films grown by different techniques, which include electrochemical, sputtering and thermal oxidation of pure metal films.[1] This work presents *in situ* Ir L_{III} edge X-ray absorption spectroscopy (XAS) data of IrO₂ films prepared by electrodeposition. As will be shown, this latter method can yield films displaying remarkably well-defined voltammetric response allowing direct correlations to be made between electrochemical and both structural and electronic properties.

EXPERIMENTAL

Iridium oxide films were electrodeposited on Au-coated Melinex using the method described in Ref. [2], yielding cyclic voltammetric curves in aqueous 0.3 M Na₂CO₃ in excellent agreement with those reported in that work (see Fig. 1). *In situ* XAS measurements were performed at beamline 4-3 at the Stanford Synchrotron Radiation Laboratory (SSRL) using the same conditions as those specified in a prior publication.[3]

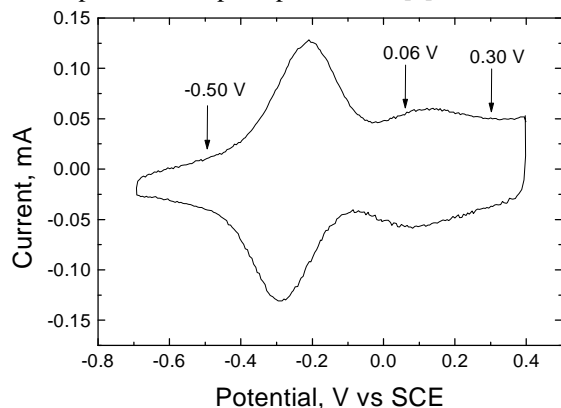


Figure 1. Cyclic voltammogram of an electrodeposited IrO₂ film in 0.3 M Na₂CO₃ at a scan rate of 20 mV/s.

RESULTS AND DISCUSSION

Fig. 2 shows *in situ* Ir L_{III}-edge XANES in the white line region, recorded at the potentials specified by the arrows in Fig. 1, which correspond nominally to the material in its three distinct oxidation states, +3, +4, and +5. These curves show a monotonic shift of the peak position $E(W_L)$ toward higher binding energies as the potential was made more positive, suggesting an increase in the oxidation state of Ir sites in the film.

Similar *in situ* Ir L_{III}-edge data have been reported by other workers for sputtered IrO₂ films. In particular, Huppaufl and Lengeler[1] studied IrO₂ films prepared by anodic oxidation of sputtered metallic Ir in 1 N H₂SO₄. Based on values of $E(W_L)$ and using Ir oxalate and Ir oxide as standards for Ir(+3) and Ir(+4) oxidation states these authors concluded that the valence over the entire voltammetric region examined varied between 3 and 4.8. More recently, Poporte et al.[4] failed to obtain evidence for the presence of Ir in a high oxidation state for films prepared by sputtering Ir in oxidizing plasma in 1 M H₂SO₄.

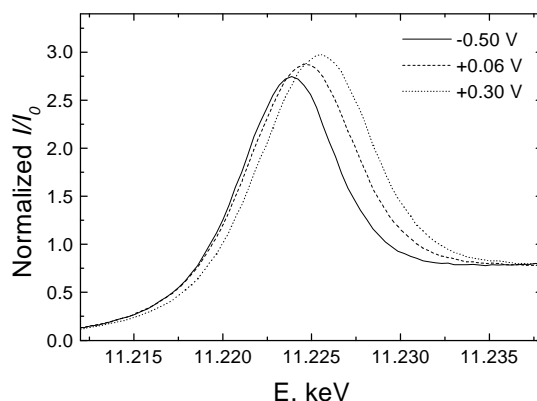


Figure 2. Ir L_{III}-edge XANES in the white line region, at the potentials specified by the arrows in Fig. 1.

The better-defined voltammetric behavior obtained in this work allows more rigorous correlations to be made between $E(W_L)$ and the state of charge of the film. As shown in Fig. 3, a plot of $E(W_L)$ vs charge yielded two linear regions of different slopes with the change in the slope occurring very close to the onset potential for the second voltammetric peak. This provides evidence that there are at least two redox processes involved and also that linear extrapolations over the entire potential range may not be warranted.

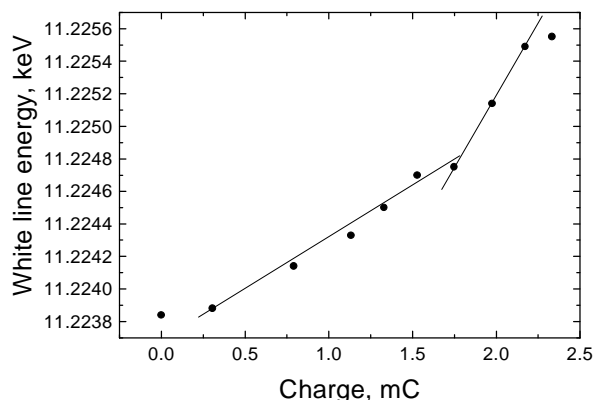


Figure 3. Variation of the white line peak position as a function of charge passed at the electrode

Support for these two oxidation states is given by the analysis of extended X-ray absorption fine structure (EXAFS). In particular, the Fourier transform of the EXAFS function acquired at the three potentials specified in Fig. 1 yielded a prominent shell attributed to the Ir-O interaction with two additional shells of significantly lower amplitude at higher r' values, which were not considered in this analysis. The analysis of the EXAFS yielded a slight decrease in the Ir-O distance from 2.02 to 1.98 and then to 1.93 Å as the material was oxidized in sequence from the more negative potentials. In particular, the Ir-O distance for the spectrum obtained at +0.06 vs SCE was identical to that obtained for XRD data of IrO₂ crystals[5], i.e. 1.98 Å. On this basis, it seems reasonable to suggest that IrO₂ is reduced and oxidized by a single electron transfer at the more negative and positive potentials, respectively.

ACKNOWLEDGMENTS

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